DOE/MC/31175 -- 5226
(DE96004501)

Treatment of Metal-Laden Hazardous Wastes with Advanced Clean Coal Technology By-Products

Quarterly Report
May - August 1995

November 1995

Work Performed Under Contract No.: DE-AC21-94MC31175

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Pittsburgh
1137 Benedum Hall
Pittsburgh, Pennsylvania 15261

Disclaimer

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DOE/MC/31175 -- 5226
(DE96004501)
Distribution Category UC- 107

Treatment of Metal-Laden Hazardous Wastes with Advanced Clean Coal Technology By-Products

May - August 1995

Work Performed Under Contract No.: DE-AC21-94MC31175

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
University of Pittsburgy
1137 Benedum Hall
Pittsburgh, Pennsylvania 15261

November 1995

TABLE OF CONTENTS

EXECUTIVE SUMMARY

During the fourth quarter, six sets of samples were produced from blends of hazardous wastes and clean coal technology (CCT) by-products, which contained higher amounts of water. These are being tested to determine the level of solidification achieved by each set. An additional five dry blends of hazardous wastes and CCT by-products were mixed. These are also being used for solidification testing by the Proctor method. Twenty-eight day compressive strengths are reported for five of the six sets of samples with high water content.

The report presents further information about the by-products and hazardous wastes being used in the project. It discusses completion of the format of the database and the inclusion in it of all data collected to date. Special reports presented during the quarter include the Continuation Application, a News Release, and modification to the Test Plan. Work is progressing on the NEPA report and the Topical Report.

By-Products

Dravo Lime Company collected the final two samples of by-product for Phase One and completed the analyses of all samples.

A second attempt to acquire a fourth by-product, one from a coal-fired fluidized bed combustor, was unsuccessful. Efforts will continue to identify such a material in the next quarter.

Hazardous Wastes

The final analyses for the sixth hazardous waste - the sewage plant soil - were completed.

Hazardous Waste Treatments

A review of the results of the laboratory treatment of five hazardous wastes with the three by-products (fifteen treatment sets in all) led to the following conclusions.

(1) For only three of the sets were successful stabilizations achieved under both present and potential future regulations.

(2) For another three sets, successful stabilizations were achieved under only present regulations.

(3) For an additional three sets, successful stabilizations were nearly achieved under present regulations.

(4) For six sets, no successful stabilizations were achieved.

For all of the sets in Group 1, two of the three sets in Group 2 and one of the three sets in Group 3, a water-containing blend having a 1" to 2" slump was prepared and cast into 3" by 6" cylinders. Three sets yielded cylinders with 28-day compressive strengths between 178 and 494 psi. Two sets failed to set up and one was made just a few days before the end of the quarter.

For one of the sets in Group 1, two of the three sets in Group 2 and two of the three sets in Group 3, a dry mixture was prepared for testing according to the Proctor Method, followed by measurement of compressive strength upon curing of a maximum-density moist sample of the mixture. A modification to the Test Plan was obtained to add this new test method to the program. Only one Proctor Test had been conducted by the end of the quarter.

Laboratory Analyses and Database Development

ASTM extraction of material from the cylinders produced in the solidification tests have begun. This effort will continue into the next portion of the project.

A summer undergraduate student, supported by the National Science Foundation's Research Experience for Undergraduates Program, began to examine the materials from the cylinders produced in the solidification tests using the scanning electron microscope and the x-ray diffraction microscope.

The computerized database for the project has been fully developed. Graphical displays will be prepared for the Topical Report.

Development of Background

Five new pertinent articles were identified and six different concepts were discussed with various individuals during the quarter.

Administrative Aspects

The Test Plan was modified to add the Proctor Method for sets of by-product/hazardous wastes treatments that did not provide effective immediate stabilization.

The Continuation Application for Phase Two of the project was submitted on June 9, 1995.

A news release was issued describing the project on June 12, 1995. Three news articles had appeared by the end of the quarter.

Just prior to the end of the quarter, work was initiated on the preparation of a NEPA report on Phase Two. This report will be completed in October 1995.

Work has begun on the Topical Report for Phase One.

Plans for the "Next Quarter"

Because of the delay in initiating Phase Two, the "next quarter" will be defined as the first full quarter of Phase Two, which will end on December 30, 1995.

During the period ("quarter") from August 18, 1995 through December 30, 1995, work will continue on Tasks 3, 4, 5, 6, 7 and 8 of Phase One. The search for a fourth by-product will continue, focussing first upon the material used previously in another project by Dravo Lime Company. Mill Service, Inc. will watch for additional wastes to add to the list, particularly a paint sandblasting residue. Preparation and evaluation of the solidification of eleven combinations of wastes and by-products, begun in the fourth quarter of Phase One, will continue. The economic evaluation, NEPA report and Topical Report all will be concluded.

Phase Two will begin on September 30, 1995. The first step in carrying out the work of the second portion of the project will be the preparation of the Test Plan for Phase Two. This document will include the detailed plan for all four quarters of the year-long period to end on September 30, 1996.

INTRODUCTION

This fourth quarterly report describes work done during the fourth three-month period of the University of Pittsburgh's project on the "Treatment of Metal-Laden Hazardous Wastes with Advanced Clean Coal Technology By-Products."

Participating with the university on this project are Dravo Lime Company, Mill Service, Inc., and the Center for Hazardous Materials Research.

This report describes the activities of the project team during the reporting period. The principal work has focussed upon the production of six sets of samples with high water content for solidification testing and the mixing of five dry samples for solidification testing by the Proctor method. Twenty-eight day compressive strengths are reported for five of the six sets of samples with high water content. The report also discusses completion of the format of the database and the inclusion in it of all data collected to date. Special reports presented during the quarter include the Continuation Application, a News Release, and modification to the Test Plan. Work is progressing on the NEPA report and the Topical Report.

The activity on the project during the fourth quarter of Phase one, as presented in the following sections, has fallen into six major areas:

- Completion of by-product evaluations
- Completion of analyses of six wastes
- Initiation of eleven solidification tests
- Continued extraction and extract analysis of solidified samples
- Development of the database
- Production of reports.

BY-PRODUCTS

Acquisition and Distribution

The final two samples of by-product (the ninth and tenth samples from the Carneys Point Cogeneration Plant) were collected. Analyses of these two samples, along with full analyses of all forty by-product samples collected and presented in the Topical Report on Phase One. The project team has received word from CONSOL that detailed operational records are not collected at Carneys Point Cogeneration Plant. Thus, no records of this type are available. The project team has examined the range of values of by-product properties obtained through analysis by Dravo Lime Company. There appears to be very little variation in values of individual parameters within the ten-sample set of each by-product. Therefore the lack of detailed operational data has been deemed of no significance to the project.

Several buckets of extra by-product, which Dravo Lime Company had collected from CONSOL's Blacksville site (by-product from the Carneys Point Cogeneration Plant) and from the Tidd Station, were transferred to the Yukon Plant of Mill Service, Inc. to use in conducting solidification tests.

General Properties

The term "mixed ratio" is an unusual parameter and is used internally by, among others, Dravo Lime Company. It is that amount of by-product which will cause a gallon of water to "set up." Put into perspective, a very good mixed ratio of 13 pounds of by-product per gallon of water would be equivalent to a water-to-cement (W/C) ratio of 0.64. Typical mortar cubes are prepared with W/C ratios of 0.48 (including sand).

An important observation put forward at this time is the relative concentration of sulfides, sulfites and sulfates in the four by-products. In particular, the by-product from the Tidd Station (pressurized fluid-bed combustion) has higher levels of sulfides and sulfites when compared to those in the by-products from the Ebensburg Power Company (coal waste-fired atmospheric fluid-bed combustion) or from the coal-fired atmospheric fluid-bed combustor (the original fourth by-product), both of which contain high levels of sulfates. The different sulfur-containing anions exhibit different performances in the stabilization of metal cations. In particular, in conjunction with calcium and silicate ions, sulfates can form ettringite which is known to incorporate certain cations in the structure over an extended period of time. This is being studied in particular by Dr. David Hassett at the University of North Dakota Energy and Environmental Research Center.

Dravo Lime Company has conducted both ASTM and TCLP extractions of the by-products. While focussing on the metal cations, it also has analyzed for the presence of the sulfite anion in the leachate. This anion has been found. Sulfite is an oxygen scavenger and is of concern to the U.S. Environmental Protection Agency, since low redox potential solubilizes certain metals.

In the section below on "Waste Treatment," the use of ASTM Test Method D 698-91 for "Laboratory Compaction Characteristics of Soil Using Standard Effort (12,400 ft-lbf/ft^3 (600 kN-m/m^3))" for preparation of compacted soil-lime test specimens and of ASTM Standard Test Method D 5102-90 for "Unconfined Compressive Strength of Compacted Soil-Lime Mixtures" is described. ASTM D 698-91 specifies the method for establishing the moisture-density relationship of a soil-lime mixture. In 1993 Dravo Lime company evaluated the moisture-density relationship of two samples of by-product from the Tidd Station. The results are given in Appendix A.

When the members of the project team from the University of Pittsburgh began to mix batches for the solidification tests (described below), they were introduced to the physical characteristics of the three by-products. Their description is as follows:

- CONSOL - very fine, grey, dust like
- Tidd - very fine, reddish brown, dust like
- Ebensburg - very fine, reddish brown, dust like.

Regulatory Issues

During discussions with experts in the use of coal combustion by-products, reference has been noted to the "Beville amendment" to the RCRA legislation. This amendment concerned indemnification for some by-product producers. The amendment mandated that the U.S. Environmental Protection Agency (EPA) study utility by-products. The EPA has identified undiluted standard ash from utilities as categorically non-hazardous. If the "standard ash" is blended with other components in the waste from a combustor (such as a fluidized bed combustor), the mixture remains outside the set of categorically non-hazardous materials. It is anticipated that the EPA will have great difficulty in giving categorically non-hazardous designation to mixtures if by-products blended into hazardous wastes to stabilize those wastes are included in an even larger set. [An excellent review of this issue - and others - was given at the University of Kentucky's Ash Utilization Symposium in October. If a written version of this paper is received in time, it will be used to clarify and extend this discussion in the Topical Report.]

Fourth By-Product

In late May the midwestern office of JTM reported that it was in communication with two midwestern clients who produce coal-fired FBC by-products and also with the original eastern client (from whom the project team has been seeking by-product for six months). Both midwestern clients expressed initial hesitation in supplying material as the fourth treatment chemical for this project because of the publication of results. Also of concern was the potential for the by-product supplier to become liable for future cleanup of a site to which the treated hazardous waste was disposed.

In mid-June the midwestern office of JTM reported that it felt it was close to identifying a coal-fired FBC by-product for use on the project. In mid-July the office reported general oral agreement with this producer and the expectation of a letter shortly thereafter. At that point the source was named to the project team. Dravo Lime Company had examined this material and had on file several analyses of it, as well as a description of the boilers producing it.

Unhappily, no further communication has been received from the midwestern office of JTM and the project team has reluctantly unilaterally terminated this approach toward the fourth by-product. Three other approaches will be considered in the first quarter of Phase Two. Most likely to be contacted first will be a producer that has provided material to Dravo Lime Company for another project. The names of two other individuals who might be contacted next were provided by the midwestern office of JTM and Deborah Hassett of the University of North Dakota Energy and Environmental Research Center.

HAZARDOUS WASTES

In Appendix D of the third quarterly report, values for antimony, beryllium, thallium and vanadium were missing from the analyses of total metals and TCLP metals for the sixth hazardous waste - the sewage plant soil. Because of the lack of even this small amount of information, the decisions on treatment levels were delayed until analytical results became available in mid July. The results in mg/kg were:

	Sewage Plant Soil Analysis	
	Total Metals (mg/kg)	TCLP Metals (μg/l)
Antimony	<1.90	<20
Beryllium	0.10	<1
Thallium	<0.48	8.4
Vanadium	12.63	<10

As a result of these analyses, beryllium and vanadium have been added to the parameters of concern for this waste. Previous results had already shown that lead and zinc are also parameters of concern for this waste.

When the members of the project team from the University of Pittsburgh began to mix batches for the solidification tests (described below), they were introduced to the physical characteristics of five of the hazardous wastes. Here is their description:

- BOF Air Pollution Control Dust - very fine, black, dust like residue
- Battery Manufacturing Sludge - very dense, moist, orange sludge
- Sewage Treatment Plant Soil - moist, dark brown soil which contained small pieces of glass and rocks
- Multi-Use Industrial Site Soil - dark brown soil which contained rocks
- Munitions Depot Soil - dark brown, clay like soil containing large pieces of glass.

Note that the Incinerator Ash is not included, as it was not used in the solidification test program.

HAZARDOUS WASTE TREATMENTS

Results of the Treatment of the Sixth Waste

The results of the analyses of the nine immediate extracts and the nine 24-hour extracts for the soil from the sewage treatment plant will be provided in the forthcoming Topical Report. These results will be evaluated early in the first quarter of Phase Two.

Evaluation of Laboratory Treatments

The results of treating each of the first five wastes with the three by-products at the 10%, 30% and 50% dosage levels (1:10, 3:10 and 5:10 weight ratios) were evaluated. For nine of the sets, solidification tests were recommended using the methodology specified in the original Test Plan for Phase One. Here is a brief evaluation of each of the nine sets, written soon after they were performed and before conducting solidification tests.

Battery Manufacturing Sludge:CONSOL #1. All of the stabilization treatments attempted were successful in achieving a residue that was hon-hazardous and that met both the current and projected future land disposal restriction (LDR) treatment standards. Therefore, solidification tests should be conducted using the lowest by-product dose (10% dosage level). See the results of Test #3 in the next sub-section.

Battery Manufacturing Sludge:Tidd #2. The highest by-product dose generated a treatment residue that was non-hazardous based on the immediate TCLP extraction and that met the current LDR treatment standards. Unfortunately, this treatment residue did not meet the projected future LDR treatment standards and the extraction performed after holding the residue for 24 hours failed to confirm the immediate extraction results. In spite of these shortcomings, a solidification test should be conducted using this by-product with this waste at the highest by-product dose (50% dosage level). The "24-hour" stabilization results indicated that the residue barely failed to achieve the concentrations required to allow disposal as a non-hazardous waste under the current LDR treatment standards. See the results of Test #9 in the next sub-section.

Munitions Depot Soil:CONSOL #1. All of the stabilization treatments attempted were successful in achieving a residue that was non-hazardous and that met the current LDR treatment standards. The treatment performed with the highest by-product dose was the only one that was clearly successful in achieving the projected future LDR treatment standards (the lower doses failed to consistently meet the lead and zinc standards in the immediate and 24-hour extractions). Therefore, a solidification test should be conducted using the highest by-product dose (50% dosage level). See the results of Test #8 in the next sub-section.

Munitions Depot Soil:EPC #3. None of the stabilization treatments attempted were clearly successful in achieving a non-hazardous residue that met the current LDR treatment standards and none of the stabilization treatment residues met the projected future LDR treatment standards. The treatment performed with the highest by-product dose came close to generating a residue that was non-hazardous and that met the current LDR treatment standards (immediate extraction failed; 24-hour extraction passed). In spite of these shortcomings, a solidification test should be conducted using this by-product with this waste at the highest by-product dose (50% dosage level). See the results of Test #4 in the next sub-section.

Munitions Depot Soil:Tidd #2. The stabilization treatment performed with the highest by-product dose was the only one that achieved a non-hazardous reside that met the current LDR treatment standards. This treatment also achieved the projected future LDR treatment standards (based on the 24-hour extraction). Therefore, a solidification test should be performed using the highest by-product dose (50% dosage level). See the results of Tests #6 and #11 in the next sub-section.

Multi-Use Industrial Site Soil:CONSOL #1. All of the stabilization treatments attempted generated a residue that was non-hazardous and that met the current LDR treatment standards. None of the treatments generated a residue that met the projected future LDR treatment standards (some failed for lead; most failed for zinc). The most promising (based on the lead control achieved) appears to be the highest by-product dose and therefore a solidification test should be performed using the highest by-product dose (50% dosage level). See the results of Test #1 in the next sub-section.

Multi-Use Industrial Site Soil:EPC #3. None of the stabilization treatments attempted were clearly successful in achieving a non-hazardous residue that met the current LDR treatment standards and none of the stabilization treatment residues met the projected future LDR treatment standards. The treatment performed with the highest by-product dose came close to generating a residue that was non-hazardous and that met the current LDR treatment standards (immediate extraction passed; 24-hour extraction failed). Therefore, a solidification test should be conducted using this by-product with this waste at the highest by-product dose (50% dosage level). See the results of Test #10 in the next sub-section.

Multi-use Industrial Site Soil:Tidd #2. The stabilization treatment performed with the highest by-product dose was the only one that achieved a non-hazardous residue that met the current LDR treatment standards. Although this treatment failed to achieve the projected future LDR treatment standards, a solidification test should be performed using the highest by-product dose (50% dosage level) based on the success in meeting the current standards. See the results of Tests #2 and #7 in the next sub-section.

BOF Dust:CONSOL #1. None of the stabilization treatments attempted were clearly successful in achieving a non-hazardous residue that met the current LDR treatment standards and none of the stabilization treatment residues met the projected future LDR treatment standards. The treatment performed with the highest by-product dose came close to generating a residue that was non-hazardous and that met the current LDR treatment standards (immediate extraction failed; 24-hour extraction passed). Therefore, a solidification test should be conducted using this by-product with this waste at the highest by-product dose (50% dosage level). See the results of Test #5 in the next sub-section.

Solidification tests using the methodology on the original test plan were not recommended for the other six sets. None of the stabilization treatments attempted were successful in achieving a non-hazardous residue and none of the stabilization treatment residues met either the current or projected future LDR treatment standards. Here is the list of those six sets.

Battery Manufacturing Sludge:EPC #3.

BOF Dust:EPC #3.

BOF Dust:Tidd #2.

Incinerator Ash:CONSOL #1.

Incinerator Ash:EPC #3.

Incinerator Ash:Tidd #2.

For these six sets, solidification tests under a modification to the original test plan were proposed on June 3, 1995 and approved on June 30, 1995. The basis for the modification was the observation that by-products from advanced clean coal technologies contain large amounts of two components that waste lime products, currently used by Mill service, Inc., lack.

- Pozzolanic precursors which slowly build cementitious structures into the composite product of hazardous waste treatment

- Sulfates which combine with pozzolans to slowly build ettringite crystals into the composite product of hazardous waste treatment.

The hazardous waste treatment business that Mill Service operates must use treatment chemicals that immediately stabilize metals. The company can ship (with a tipping fee to a regular landfill) only treated wastes whose characteristic hazard has been eliminated. A treatment chemical which requires some days to remove the characteristic hazard is not economically useful to Mill Service. Thus, only immediate stabilization has been examined so far in our tests.

However, the project team sees the possibility that an economically successful hazardous waste treatment business might be devised in which treatment of hazardous waste is obtained using a slow stabilization chemical. The economics would be obtained if the treated waste, after proof of its having become characteristically non-hazardous by the end of a "curing" time, would be sold as a structural fill to a nearby construction project. For a use such as this, a "successful" treatment chemical will stabilize the metals within a reasonable curing time (28 days or less).

The Test Plan at the beginning of the quarter called for examining the concretization of treated wastes obtained only by immediately successful recipes. Such materials would be useful in grouts. The project team decided to expand its examination to include the determination of successful slow stabilization recipes and the compaction (as a soil-like material) of treated wastes obtained by these slow successful recipes. Such materials would be useful in structural fills, pavement bases and subbases, and stabilized subgrades.

Specific methods for solidification testing of the immediately unsuccessful recipes include production of 4" or 6" diameter cylinders by ASTM Test Method D 698-91 (the so-called Proctor Test) and then curing the cylinders and testing their compressive strength by ASTM Test Method C 311-87a.

The exact statement of the modified solidification test was added to Page 16 of the Test Plan:

> For each unsuccessful combination of waste and by-products (the remaining combinations of the 40 combinations in all) a set of small-scale samples will be prepared at MSI and tested at Pitt for leachable (TCLP) concentrations to determine the rate of slow stabilization and the possibility of full stabilization within a reasonable "curing" time. For each successful slow stabilization, a set of 4" diameter cylinders will also be prepared at Pitt and, after curing, tested there for compressive strength and shear.

A copy of the letter, which approved this change, is included as Appendix B.

Solidification Tests

Before preparing the first cylinders for the recipes that were immediately successful in meeting both current and possible future regulations, it was estimated that 50 pounds of dry mixture would be required to fill 25 3-inch by 6-inch cylinders. For example, if a 1:10 by-product:waste recipe (10% dosage level of by-product into the waste) was desired, 4.5 pounds of by-product would be blended with 45 pounds of the waste. [Because of confusion in interpretation, Test #2 was prepared with the ratio of 5:5 (or 10:10) instead of 5:10.]

For the recipes that were immediately successful in meeting current regulations but were not immediately successful in meeting possible future regulations, that were to be prepared by the Proctor method, it was estimated that 90 pounds of dry mixture would be required in order to prepare 20 4-inch by 4.6-inch cylinders [5 for moisture-density determinations and approximately 15 for compressive strength testing]. Therefore, 30 pounds of by-product would be blended with 60 lbs of waste to obtain a 50% dosage. [Again, because of confusion in interpretation, Test #7 and #8 were prepared at a ratio of 10:10 instead of 5:10].

For each of the recipes that were immediately successful in meeting both current and possible future regulations, as well as for three that were immediately successful (or nearly successful) in meeting current but not possible future regulations, a water-containing blend having a 1" to 2" slump was prepared. This mixture was prepared by placing a measured weight of by-product into a 32" x 21" x 9" plastic mortar box. Large particles such as rocks and glass were removed from the waste by passing the material through a 3/4" sieve [ASTM C 192-90a (Practice for Making and Curing Concrete Test Specimens in the Laboratory) states that the diameter of cylindrical specimens shall be at least three times the nominal maximum size of the coarse aggregate in the concrete]. A measured weight of sieved waste was then added to the mortar box and the mixture blended with a cement hoe until well mixed in consistency and color. A measured volume of water was then added to the mixture and blended until well mixed. This step was repeated if the mix was too dry. The slump of the mixture was tested as per the requirements of ASTM C 143-90a (Test Method for Slump of Hydraulic Cement Concrete). In this test, a sample of the freshly mixed grout is placed and compacted by rodding in a mold shaped as the frustum of a cone. The mold is raised, and the mixture allowed to subside. The distance between the original and displaced position of the center of the top surface of the mixture is measured and reported as the slump. If the slump was not in the desired range of 1 - 2", the mixture was adjusted by adding more water if the mixture was too dry, or adding proportional amounts of waste and by-product if the mixture was too wet. Once the desired slump was obtained, the mixture was compacted into 3"x6" diameter cylinders as per ASTM C 192-90a. This procedure involved placing the material into the molds in three equal layers and consolidating each layer by rodding 25 strokes with a 5/8" diameter tamping rod. After consolidation the surface was struck off with a trowel to produce a flat surface level with the edge of the mold. After finishing, the specimens were covered with plastic in order to prevent moisture loss and stored for 48 hours. Additionally, a sample of approximately 500 grams was returned to Pitt in order to undergo ASTM extraction for heavy metals leachability according to ASTM D 3987-85 (Test Method for Shake Extraction of Solid Waste With Water). Following the 48 hour setup period, the samples were transported to Pitt, the molds were stripped, and the specimens placed in a moist room to cure.

A summary of the solidification tests prepared to date using this methodology is:

Test # and Date Prepared	Mixture Type	Weight By-Product (lbs)	Weight Waste (lbs)	Mixture Ratio	Water Added (liters)	Slump (inches)
#1 6/27/95	CONSOL/ Battery Sludge	15	45	3.3:10	0	2.0
#2 6/27/95	Ebensburg Munitions Soil	30	30	10:10	6.8	1.5
#3 7/11/95	Tidd/ Industrial Soil	22	44	5:10	4.0	1.25
#4 7/17/95	CONSOL/ Munitions Soil	25	50	5:10	7.5	1.5
#5 7/17/95	Tidd/ Battery Sludge	32.5	45	7.2:10	0	2.0
#6 8/15/95	Tidd/ Munitions Soil	22.5	45	5:10	4.0	1.5

Following specified curing times of 3, 7, 14, 28, and 90-days the compressive strength of the above solidification mixtures was evaluated according to ASTM C 39-86 (Test Method for Compressive Strength of Cylindrical Concrete Specimens). When possible, samples were capped with sulfur mortar prior to testing according to ASTM C 617-87 (Practice for Capping Cylindrical Concrete Specimens) in order to provide plane surfaces on the ends of the cylinders. Samples that did not undergo significant solidification were not able to be capped.

Compressive strengths (in psi) for cylinders from tests #2, #3, and #5 are shown in the following table.

Curing Time (days)	Test #2	Test #3	Test #5
3	29	39	35
7	295	82	61
14	433	153	138
28	494	217	178

The cylinders from Test #1 and #4 developed negligible compressive strengths. The cylinders from Test #6 were just beginning to cure as the quarter ended.

For those recipes that were immediately successful in meeting current regulations but were not immediately successful in meeting possible future regulations,[1] a dry mixture consisting of 50% by-product to waste was prepared, placed in 5-gallon buckets, and transported to Pitt for evaluation by the so-called Proctor method [ASTM D 698-91 (Test Method for Laboratory Compaction Characteristics of Soil Using Standard Effort (12,400 ft-lbf/ft^3 (600 kN-m/m^3))]. In this test, a material at a selected water content is placed in three layers into a mold with dimensions of 4.0 inch diameter and 4.584 inches height, with each layer compacted by 25 blows of a 5.5-lbf rammer dropped from a height of 12 inches producing a compactive effort of 12,400 ft-lbf/ft^3. The resulting dry unit weight is determined. The procedure is repeated for a sufficient number of water contents to establish a relationship between the dry unit weight and the water content for the soil. This data, when plotted, represents a curvilinear relationship known as the compaction curve. The values of optimum water content and standard maximum dry unit weight are determined from the compaction curve.

Following determination of the optimum water content, 12 specimens are prepared at the optimum water content so unconfined compression testing can be performed on laboratory cured specimens of 14, 28 and 90 day ages according to ASTM D 5102 (Test

[1] It should be noted that for several recipes that were immediately successful in meeting both present and possible future regulations dry mixes for evaluation by the so-called Proctor method were also prepared. This was done to provide a comparison of the two solidification methods.

Method for Unconfined Compressive Strength of Compacted Soil-Lime Mixtures). These samples are prepared using the same equipment and procedure as specified above for construction of the compaction curve. Following curing periods of 28 and 90 days, a TCLP is prepared in order to evaluate the success of long-term stabilization .

As of the completion of this quarter, only one mixture has been prepared using this methodology. A dry mixture consisting of 50 lbs of CONSOL by-product and 50 lbs of the Industrial Soil was prepared on June 27, 1995, placed in plastic buckets, and returned to Pitt. Construction of the compaction curve was performed on June 29, and the Optimum Moisture Content was found to be 31%. A copy of the moisture-density data and the compaction curve is included in Appendix C. Preparation of the samples for compressive strength testing was completed on July 10. The 14-Day strength of this mixture was 101 psi. Additionally, a dry mixture of Tidd by-product and the Industrial Soil (10:10) was prepared on June 27, but a poor compaction curve was obtained and there was insufficient sample to repeat the procedure and mold compressive strength specimens. Three other dry mixtures have also been prepared, but complete construction of the compaction curve had not been completed at the end of this quarter. A summary of the solidification tests prepared to date using this methodology is as follows:

Test # and Date Prepared	Mixture Type	Weight By-Product (lbs)	Weight Waste (lbs)	Mixture Ratio	Optimum Moisture Content (%)
#7 6/27/95	CONSOL/ Industrial Soil	50	50	10:10	31
#8 6/27/95	Tidd/ Industrial Soil	50	50	10:10	Insufficient Sample to Determine
#9 7/11/95	CONSOL/ BOF Dust	40	80	5:10	Analysis Incomplete
#10 7/11/95	Tidd/ Munitions Soil	40	80	5:10	Analysis Incomplete
#11 8/15/95	Ebensburg/ Industrial Soil	30	60	5:10	Analysis Incomplete

LABORATORY ANALYSES AND DATABASE DEVELOPMENT AT THE UNIVERSITY OF PITTSBURGH

The three samples of each by-product which were given full analyses by Dravo Lime Company were digested for total metals analyses and extracted by the TCLP method for leachable metals analyses. The results will be provided in the forthcoming Topical Report.

ASTM extractions of cylinders from the solidification tests began in July. This work requires a large number of analyses. Those that are complete by September 30, 1995 are reported in the Topical Report. Further analyses will be obtained and reported during Phase Two.

Two undergraduate students joined the project team during this quarter. One, Jana Agostini, a senior in the Chemical and Petroleum Engineering Department of the University of Pittsburgh, assisted in developing the database and in initiating the design of a high pressure permeameter to evaluate the diffusion of water through the concrete cylinders prepared during the solidification testing portion of the project. Ms. Agostini has spoken with two faculty, one graduate student and one technician of the Civil and Environmental Engineering Department with expertise in this area. A preliminary design of the equipment needed for this study has been developed. Ms. Agostini will continue developing the permeameter during Phase Two.

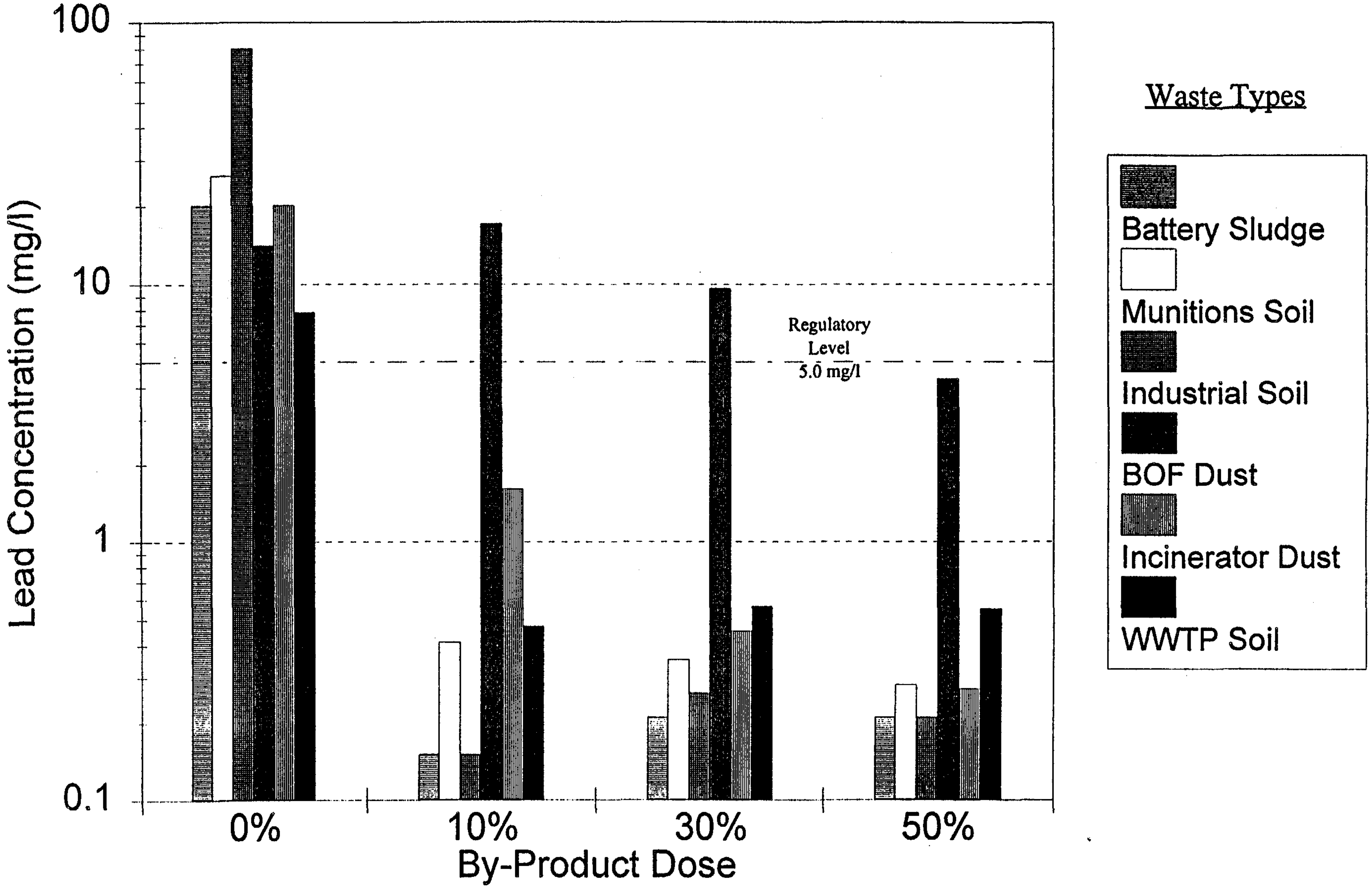
The other undergraduate student, Clarence Murray, spent the summer at the University of Pittsburgh under the support of the National Science Foundation as a participant in the program providing "Research Experience for Undergraduates" - "REU." The Chemical and Petroleum Engineering Department at the University of Pittsburgh has organized and operated an REU site for the past two years. Mr. Murray is a sophomore in the Chemistry Department of Norfolk State University. As an REU student, Mr. Murray studied the "Evaluation of Crystal Growth in Treated Metal Laden Waste by X-ray Diffraction and the Scanning Electron Microscope." His report on his work during the summer is included as Appendix D.

Much effort has been devoted during the quarter to developing the computerized database for the project. Some key decisions made along the way have been to

- List all values observed below the level of detection (LD) as "<LD" but plot them as "LD" on all graphs.
- Place lines at the level of detection and at the regulatory level on all graphs.
- Consolidate the by-product, waste, treated waste stabilization, and treated waste solidification data in separate spreadsheet "notebooks." Present the data for individual by-products, wastes and treated wastes in separate "sheets" of their respective "notebooks."
- Maintain the QA/QC data in a separate "notebook" but do not include it in the Topical Report.

An example of the graphical displays that will be prepared for the Topical Report is given on the next page. In this figure is shown the lead concentration in the 24-hour TCLP extracts of the six untreated wastes and the wastes treated with three dosages of the CONSOL by-product. It clearly shows that, except for the two lower dosages applied to the BOF dust, all dosages of the CONSOL by-product drops the lead concentration in the extracts below the 5.0 mg/l current regulatory level.

Lead Concentration in Wastes Treated With CONSOL By-Product
24-Hour TCLP



TREATWST.WB1

DEVELOPMENT OF BACKGROUND

Several articles were identified as being pertinent and useful for the project:

- "Laboratory Determination of Engineering Properties of Dry FGD By-Products," W. E. Wolfe and J. H. Beeghly, paper presented at the Ninth Annual International Pittsburgh Coal Conference, Pittsburgh, October 12-15, 1992.

- "Truck Ramp Construction from Clean Coal Technology Waste Products," W. E. Wolfe and J. H. Beeghly, paper presented at the Symposium on Recovery and Effective Reuse of Discarded Materials and By-Products for Construction of Highway Facilities, Denver, October 19-22, 1993.

- "Standard Guide for the Use of Coal Combustion Fly Ash in Structural Fills," draft of ASTM Committee E-50 on Environmental Assessment, Subcommittee 50.03 on Pollution Prevention, Reuse, Recycling, and Environmental Efficiency, December 6, 1994.

- "Advanced Emissions Control Brings Coal Back to New Jersey - Carneys Point Generating Plant," Power, Pages 24 and 26, April 1994.

- "No Change Expected in Part 503 Cadmium Limit," Biocycle, Page 8, May 1995.

A number of discussions were held with various individuals on pertinent aspects of the project. Concepts addressed in these conversations include:

- Use of additives, such as calcium mono-phosphate, silica fume, soluble silicates, Portland cement, Class C fly ash, lime kiln dust, and dolomitic lime to modify stabilization and solidification.

- Potential for fundamental studies on trapping, encapsulation, fusion, etc. as mechanisms of stabilization.

- Development by ASTM of two proposed standards, one already mentioned just above and the other entitled "Specification for Coal Combustion Fly Ash Used for Solidification of Waste" which would address the use of coal fly ash (and other CCBs) for the solidification of wastes and whose drafting is being funded by the American Coal Ash Association and by USWAG.

- Potential for use of transportation containers being developed by SEEC, Inc., for shipping of large amounts of by-products as required in Phase Two.

- Current regulatory requirement imposed on Mill Service, Inc., that treatment chemicals must be purchased. Any material that might be used for successfully treating hazardous waste but which must be taken in at the Yukon Plant with an associated tipping fee must be classified as a waste and is not permitted for use. The economic evaluation to be reported in the Topical Report will ignore this current limitation, for it is anticipated that all of the advanced clean coal technology by-products will require a tipping fee. An important activity of Phase Two will be giving attention to this limitation.

- Concern for utilization of severe potential limits on treatment levels under Landban, as currently used in this study. Evaluation of the treatment results by these "worst case" future standards may add unnecessarily to the uncertainty already being felt by by-product producers as they assess indemnification requirements for potential liabilities in the future.

ADMINISTRATIVE ASPECTS

This section focuses first on five specific reports. It provides the monthly highlights and then closes by comparing progress with the milestone chart.

Modification to the Test Plan

Recognizing that treatments that do not provide effective immediate stabilization may be acceptable at slow stabilization, the project team requested and received approval for modifications to the Test Plan. Under the requested changes, cylinders for certain of the waste/by-product combinations will be prepared by the ASTM Test Method D 698-91 (the Proctor method). Curing and compressive strength testing of these cylinders will proceed as usual by the ASTM Test Method C 311-87a. These modifications were discussed in an earlier section of this report.

Continuation Application

To embark upon Phase Two of the project, the project team was required under terms of the cooperative agreement to submit a Continuation Application to the Contracting Officer approximately three months prior to the final official day of the first phase. After consultation with the Contracting Officer's Representative, the project team prepared a comprehensive review of the objectives, procedures, materials and results of the activities of the first three quarters of the project. The plan for the project's fourth quarter and the rationale for proceeding to Phase Two were presented. The application concluded with a detailed description of the proposed work, a draft "statement of work", and a budget for Phase Two. The Continuation Application was submitted on June 9, 1995.

News Release

On June 12, 1995 the University of Pittsburgh issued a news release announcing the award of the contract for this project. The two-page release is presented in Appendix E. During the fourth quarter the project team learned of one article and two announcements which resulted from the release.

- "Engineers Study Treatment of Waste," The Pitt News, Volume XC, Issue 9, Pages 1 and 4, Wednesday, July 5, 1995.
- "Contracts - The University of Pittsburgh's School of Engineering," The Pittsburgh Business Times, Page 21, July 3-9, 1995.
- "Engineering School Awarded Contract from DOE," University Times, Volume 27, Number 23, Page 4, July 20, 1995.

The article and the two announcements are also reproduced in Appendix E.

NEPA Report

The final task of Phase One of the cooperative agreement is the preparation of a NEPA report on Phase Two. The contract specifies that work on the report must be initiated by a letter of approval from the Contracting Officer. An informal request for the approval letter was made by the project team in early May and a formal request was submitted to the Morgantown Energy Technology Center on July 12, 1995. The letter authorizing the NEPA study was issued by the Contracting Officer on August 14, 1995.

In anticipation of the receipt of the authorization letter, the principal investigator met with the manager of the subcontract from the Center for Hazardous Materials Research (CHMR) on June 30, 1994 to plan the steps to be taken to collect the information and documentation necessary for the study. However, no work could begin until August 14, 1995. At the end of the quarter, drafts of letters to governmental agencies for comment on Phase Two had been prepared and a meeting scheduled for the project team from CHMR to visit the Yukon Plant of Mill Service, Inc. to begin collecting information at the commercial site for Phase Two.

Topical Report

Preliminary work began on the topical report for Phase One in late July. Major topics to be covered were identified.

- Background on advanced clean coal technology by-products, characteristic metal-laden hazardous wastes, stabilization of metal-laden hazardous wastes, and solidification of fine aggregate with mixtures of pozzolans, lime and sulfite/sulfate materials.

- Rationale, approach and methodology of the project.

- Detailed record of work on the project.

- Detailed listing of the data obtained.

- Graphical displays of the data for use in the analysis to follow.

- Analysis of the data, comparing the performance of the treatment products with each other and with that of other investigators (such as those at the University of Kentucky and the University of North Dakota), and discussing how the fundamental behavior of materials such as these explains the data we've obtained.

- Economic and commercial potential of the use of these advanced clean coal technology by-products for the treatment of characteristic metal-laden hazardous waste; this analysis should include a detailed examination of regulation and indemnification.

- Conclusions and recommendations.

- Plan for Phase Two.

As the quarter ended, the project team was beginning to give thought to the contents under these topics. In particular, Mill Service, Inc. was working on a first draft of the economic evaluation. The evaluation will begin by examining the values the they place upon the three by-products examined in Phase One in order to maintain its profit margin. The values may be positive (Mill Service will purchase them) or negative (Mill Service will charge for receiving them).

Monthly Highlights

Here are the highlights of the fourth three months of the first phase of the project.

May 18 - June 18, 1995

- Laboratory treatments are evaluated.
- Solidification test plan is devised.
- Continuation Application is submitted.
- News Release is issued by the University of Pittsburgh.

June 18 - July 18, 1995

- Five solidification tests with high water contents are initiated.
- Modifications to the Test Plan are approved.
- Four dry mixes are prepared for Proctor testing.
- Final metals analyses are completed on the sixth waste and its treatment products.
- Database is fully developed and current.
- Articles appear in three newspapers in response to the News Release.

July 18 - August 18, 1995

- One solidification test at high water content is initiated.
- One dry mix is prepared for Proctor testing.
- First compressive strengths from solidification tests with high waster contents show the Ebensburg by-product to be very effective, that from Tidd less so, and the by-product from CONSOL ineffective.

- First Proctor test shows the optimum moisture content for the CONSOL/Industrial Soil combination to be 31%.

- CONSOL/Industrial Soil combination with 31% moisture reaches a compressive strength of 101 psi at 14 days.

- Economic evaluation is initiated.

- Authorization is received to begin the NEPA evaluation of Phase Two.

- Work is initiated using the X-ray Diffraction and Scanning Electron Microscopes by a summer student in the Research Experience for Undergraduates Program.

Comparison of Progress with Milestone Chart

The following tasks were scheduled for completion during the fourth quarter of Phase One:

- Task 1 - Literature Review

- Task 3 - Sample Collection and Characterization

- Task 4 - Treatment of Metal-Laden Waste with CCT Solid By-Product

- Task 5 - Data Analysis

- Task 6 - Economic Analysis

- Task 8 - Information Required for the National Environmental Policy Act (NEPA)

Task 1 was finished during this period. By submitting the Continuation Application on June 9, 1995 and the Third Quarterly Report on July 11, 1995, the project team met two of its reporting requirements for this period.

The third reporting requirement, Task 8, could not be completed because of the lateness of the receipt of the authorization letter. It will be submitted on or about October 31, 1995.

The Topical Report, Task 7, which was due on October 18, 1995, has been delayed for approximately one month because of uncertainty through mid-September over the final date of the end of Phase One. The project team was told in mid-August that Phase One would be extended to the end of the calendar year. However, in mid-September it was informed that Phase Two would begin on September 30, 1995, but there was no indication that Phase One extended to that date.

During the month of uncertainty over the date of the end of Phase One, the pace of work on Tasks 5 and 6 also was slowed significantly. They will be completed for inclusion in the Topical Report.

The identification of the fourth by-product and of the final four wastes has continued to be stalled. A report on the problems associated with the fourth by-product were noted in a previous section. Additional wastes still have not appeared at MSI. It was thought at one point during the quarter that a waste from sandblasting of paint from structures was on its way to the Yukon Plant, but that report proved incorrect. Thus, the work on Task 3 will continue into Phase Two.

Laboratory treatments using the wastes and by-products in hand have been completed. The solidification studies based upon all eighteen possible waste/by-product combinations are being conducted at a pace such that they will be fully completed by the end of the calendar year. If and when the fourth by-product and the last four wastes are identified, laboratory evaluation of their use in stabilization and solidification will be conducted. Thus, the work on Task 4 will continue into Phase Two.

PLAN FOR THE NEXT "QUARTER"

Phase One officially ended on August 18, 1995, but work scheduled for Phase One will continue through the hiatus between its end and the beginning of Phase Two on September 30, 1995. The next quarter for reporting purposes will end on December 30, 1995.

During the period ("quarter") from August 18, 1995 through December 30, 1995, work will continue on Tasks 3, 4, 5, 6, 7 and 8 of Phase One. The search for a fourth by-product will continue, focussing first upon the material used previously in another project by Dravo Lime Company. Mill Service, Inc. will watch for additional wastes to add to the list, particularly a paint sandblasting residue. Preparation and evaluation of the solidification of eleven combinations of wastes and by-products, begun in the fourth quarter of Phase One, will continue. The economic evaluation, NEPA report and Topical Report all will be concluded.

Phase Two will begin on September 30, 1995. The first step in carrying out the work of the second portion of the project will be the preparation of the Test Plan for Phase Two. This document will include the detailed plan for all four quarters of the year-long period to end on September 30, 1996.

APPENDIX A

RESULTS OF PROCTOR TEST USING TIDD BY-PRODUCT

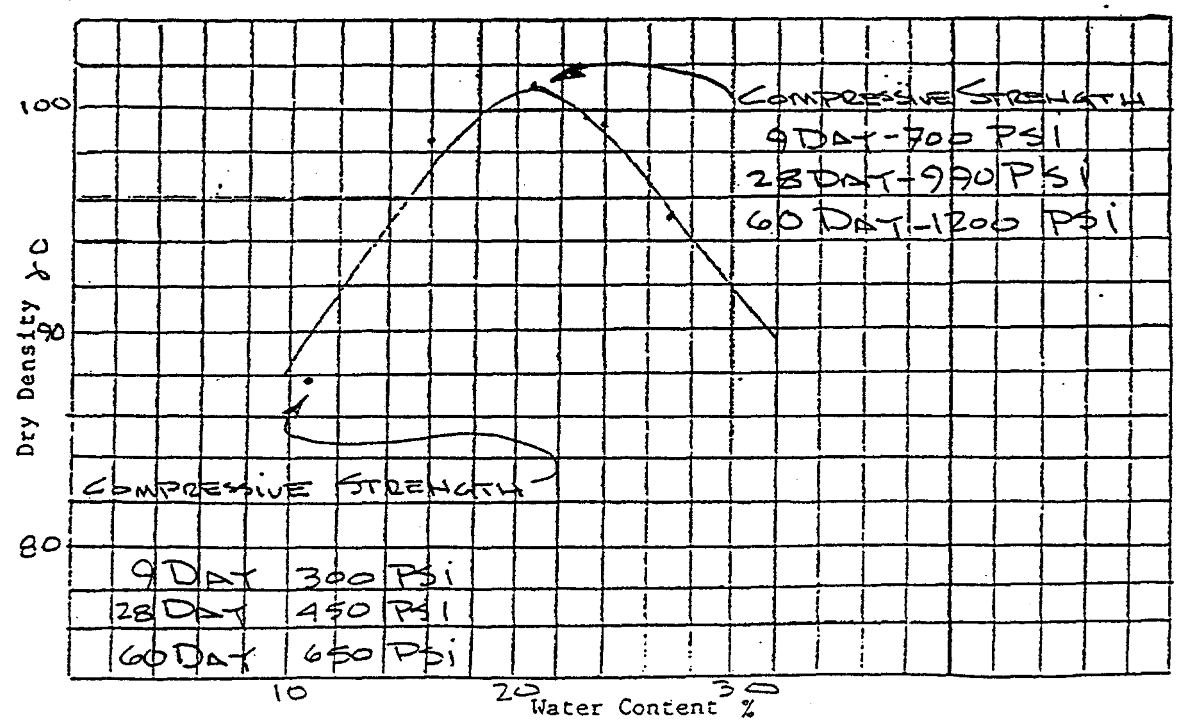
DRAVO CORPORATION
MOISTURE-DENSITY RELATIONSHIP

~6/9/95

Project No. TIDD PFBC SAMPLED 7/22/93 Tested by: ST / 7/22/93
Sample No. 1 BED ASH TO 2 FLY ASH BY VOLUME Calc. by:
Sample Description BLENDED + CONDITIONED @ LAND FILL SITE Checked by:

WT MOLD + WS										
WT MOLD										
WT WS.	3.24		3.82		4.08		4.12		4.00	
VOL MOLD	1/30		1/30		1/30		1/30		1/30	
WET γ Pcf	97.2		114.6		122.4		123.6		120.0	
TARE NO.	1		2		3		4		5	
WT TARE + WS	192.9		180.5		180.8		300.2		293.5	
WT TARE + DS	176.5		158.5		153.0		246.1		236.2	
WT TARE	20.9		20.9		20.9		20.9		20.9	
WT DS	155.6		137.6		132.1		225.2		215.3	
WT WATER	16.4		22.0		27.8		54.1		57.3	
WC	10.5		16.0		21.0		24.0		26.6	
AVERAGE WC	10.5		16.0		21.0		24.0		26.6	
γD= γ / (1+WC)	87.9		98.8		101.1		99.7		94.8	

DRY γ PCF



$$\text{Dry Density} = \frac{\text{Wet Density}}{1 + (\%\ \text{Moisture}/100)}$$

* Blows/Layer

Designation Used STANDARD
Method Used C

Method	Material Size	Mold Size	Blows*
A	All Passing #4	4" Dia.	25
B	All Passing #4	6" Dia.	56
C	All Passing 3/4"	4" Dia.	25
D	All Passing 3/4"	6" Dia	56

Designation	Ham/Drop	Layers
Standard	5.5#/12"	3
Modified	10#/18"	5

MOISTURE-DENSITY RELATIONSHIP

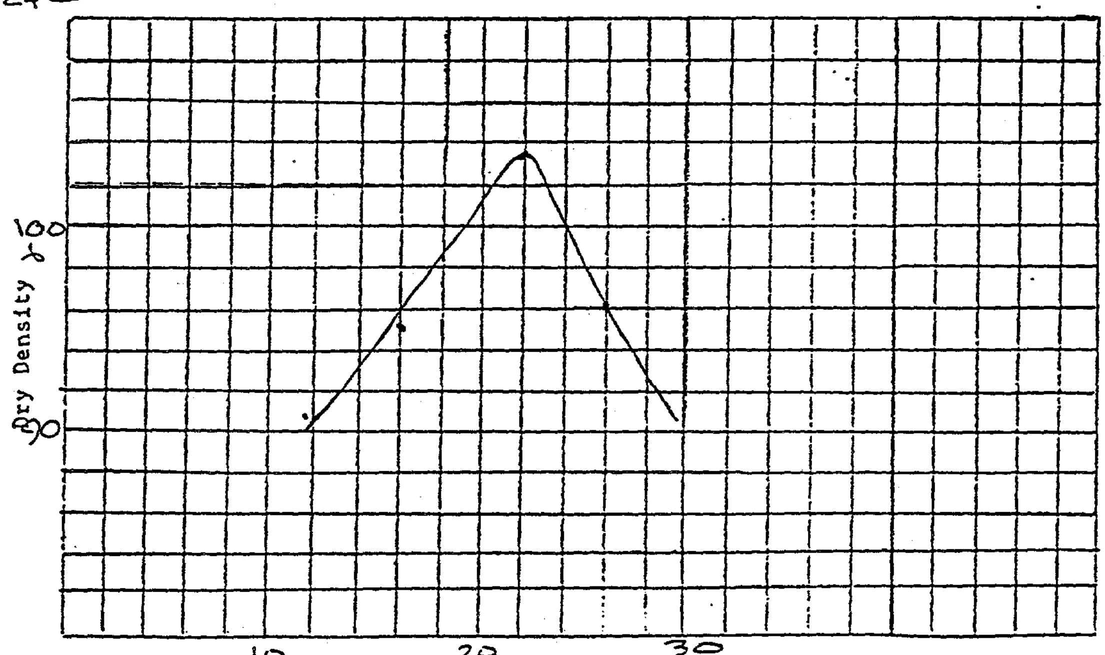
Project No. ROUTE 541 REPAIR
Sample No. TIDD SAMPLE REC'D 10/15/93
Sample Description BLENDED + CONDITIONED

Tested by: ST 10/18/93
Calc. by:
Checked by:

AS REC'D MOISTURE 14.3%

WT MOLD + WS					
WT MOLD	10.40	10.40	10.40	10.40	
WT WS.	3.37	3.68	4.12	4.02	
VOL MOLD	1/30	1/30	1/30	1/30	
γ	101.1	110.4	123.6	120.6	
TARE NO.	1	2	3	4	
WT TARE + WS	210.5	180.5	190.3	185.8	
WT TARE + DS	192.7	158.5	160.1	151.9	
WT TARE	20.8	20.8	20.8	20.8	
WT DS	171.9	137.7	139.3	131.1	
WT WATER	20.8	22.0	30.2	33.9	
WC	12.1	16.0	21.8	25.9	
AVERAGE WC					
$\gamma D = \gamma / (1+WC)$	90.2	95.2	101.5	95.8	

Dry γ Pcf



$$\text{Dry Density} = \frac{\text{Wet Density}}{1 + (\text{\% Moisture}/100)}$$

Method	Material Size	Mold Size	Blows*
A	All Passing #4	4" Dia.	25
B	All Passing #4	6" Dia.	56
C	All Passing 3/4"	4" Dia.	25
D	All Passing 3/4"	6" Dia.	56

* Blows/Layer

Designation Used STANDARD
Method Used C

Designation	Ham/Drop	Layers
Standard	5.5#/12"	3
Modified	10#/18"	5

APPENDIX B

LETTER APPROVING CHANGES IN TEST PLAN

Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
3610 Collins Ferry Road
Morgantown, West Virginia 26507-0880

June 30, 1995

James T. Cobb, Jr., Ph.D.
Energy Resources Program
University of Pittsburgh
1137 Benedum Hall
Pittsburgh, PA 15261

Dear Dr. Cobb:

I have reviewed your requested Test Plan modifications for Cooperative Agreement DE-FC21-94MC31175. Provided there is no resultant change to the scope of work, total cost, or time required for Cooperative Agreement performance, your request seems appropriate. Specifically, I believe the recommended investigation into the long-term ability to stabilize metal-laden hazardous waste of the by-products that proved ineffective in immediate stabilization has technical merit and could subsequently lead to an economically feasible commercial use. However, I do have the following concerns:

- As you pointed out, only treatment chemicals that provide immediate stabilization are currently economical in the hazardous waste treatment industry. Your assumption that the economic benefit from the potential use of by-products that require a "cure" period for stabilization to be successful may be essentially true. However, I believe the issue for companies such as Mill Service is the potential cost and liability that would be associated with committing the necessary space, facilities, and other resources necessary to contain, control, and monitor the "curing" materials relative to the economic benefit they could reasonably expect to gain from their subsequent use as a structural fill material.

- What you consider to be a "reasonable" curing time was not clearly evident. I suspect your economic analysis will affect the determination of what is reasonable.

This technical direction is offered in accordance with Section B, Part II, 2.(a) of the Cooperative Agreement. It does not constitute acceptance or agreement on potential cost or schedule impacts. You are not to proceed with any change that impacts the scope of work, total cost, or the time required for Cooperative Agreement performance without obtaining prior written authorization from the Contracting Officer, Mr. Gerald W. Bolyard. If however, there is no such impact, you have the right to conduct the project at your discretion to meet

TELEPHONE: (304) 285-4724 • FA: (304) 285-4403 • E-MAIL: lewis@wposmtp.metc.doe.gov

the terms and conditions of the Cooperative Agreement.

Should you require further assistance, please contact me at (304) 285-4724.

Sincerely,

Jason T. Lewis
Project Manager,
Environmental and Waste
Management Division

3

cc: T. L. Martin
G. W. Bolyard

APPENDIX C

RESULTS OF PROCTOR TEST FOR A CONSOL/INDUSTRIAL SOIL BLEND

UNIVERSITY OF PITTSBURGH

SOILS MECHANICS LABORATORY

COMPACTION TEST

Soil Sample Description CONSOL / Industrial Soil Sample 5:5

Location

Boring No. Sample Depth

Sample No. Test No.

Field Water Content 7.1 % Specific Gravity

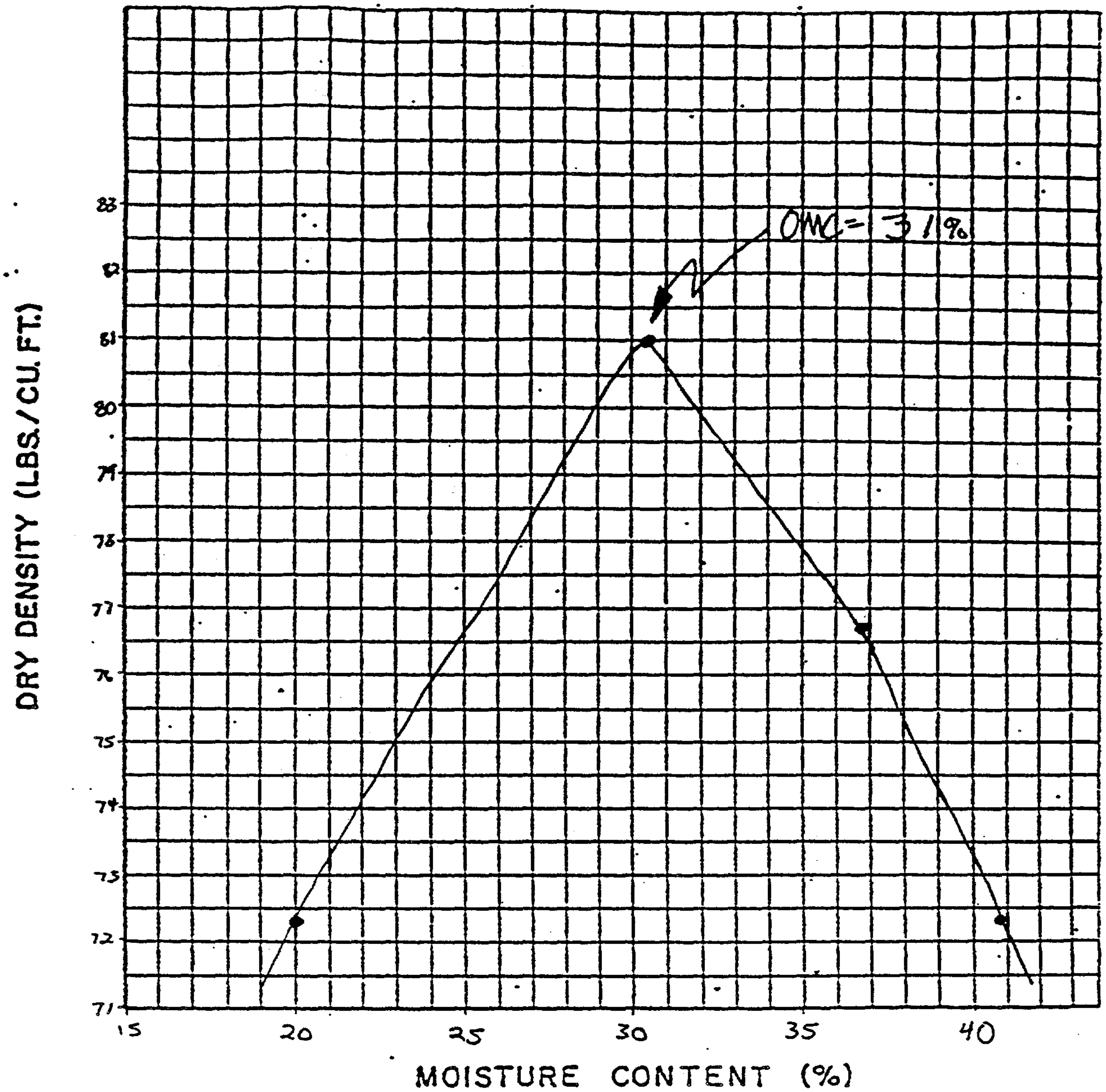
Date 6/29/95 Tested By J. Pritts

DENSITY

Determination No.	1	2	3	4	5
Wt. of mold + Comp. Soil (gm)	12.44	13.01	12.84	12.96	
Weight of Mold (gm)	9.55	9.49	9.35	9.57	
Weight of Compacted Soil (gm)	2.89	3.52	3.49	3.39	
Wet Density, γ (pcf)	86.8	105.7	104.8	101.8	
Dry Density, γ_d (pcf)	72.3	81.0	76.7	72.3	
Void Ratio, e					
Porosity, n					

WATER CONTENT

Determination No.	1	2	3	4	5
Container No.	1	2	3	4	
Weight of Container (gm)	75.42	71.22	86.21	72.18	
Weight of Container + Wet Soil	160.36	175.70	203.11	204.38	
Weight of Container + Dry Soil	146.21	151.29	171.82	166.08	
Weight of Water, W_w (gm)	14.15	24.41	31.29	93.90	
Weight of Dry Soil, W_s (gms)	70.79	80.07	85.61	38.30	
Water Content, w%	19.99	30.49	36.55	40.78	



JOB: CONSOL / Industrial Soil
DATE TESTED: 6/29/95

HOLE NO.	SAMPLE NO.	ω_n%	$\omega_{opt.}$%	γ_d (max)pcf	METHOD OF TESTING
	1	20.0		72.3.	
	2	30.5		81.0	
	3	36.6		76.7	
	4	40.8		72.3	

APPENDIX D

RESEARCH EXPERIENCE FOR UNDERGRADUATES PROGRAM REPORT BY CLARENCE MURRAY

CLARENCE W. MURRAY, III
Norfolk State University
Advisor: Dr. James T. Cobb Jr.
Department of Chemical and Petroleum Engineering
Co-Advisor: Dr. Ronald D. Neufeld
Department of Civil & Environmental Engineering

EVALUATION OF CRYSTAL GROWTH IN TREATED WASTE BY X-RAY DIFFRACTION AND THE SCANNING ELECTRON MICROSCOPE

The project entitled "Evaluation of Crystal Growth in Treated Waste by X-ray Diffraction and the Scanning Electron Microscope" was performed using characteristic metal-laden hazardous wastes from various landfills that were treated by the process of stabilization. The typical way to stabilize such waste is by adding lime to it. A new source of low-cost lime has been proposed from Advanced Clean Coal Technologies. This new source of lime is the slate of residues from fluid bed combustors and also from dry scrubbers which clean the flue gas from pulverized coal boilers.

The purpose of this project was to develop a better understanding of crystal growth in wastes stabilized with these new residues (by-products); to recognize which by-product developed the most well-defined crystal over a 28 day aging period and possibly to identify the crystal formation. The importance of this overall program, of which this project is part, is that it may allow the recycling of the treated waste materials by producing sufficient crystalline growth for beneficial solidification of the waste. X-ray Diffraction was vital to the search for crystal growth in the project because it provided the procedures necessary for identifying the types of crystalline growth. The Scanning Electron Microscope was useful because it provided an image of the topography of the stabilized waste surface to identify specific locations of those crystals.

Overall, the crystal growth in these stabilized wastes varied from one to another, apparently because of the percentage of lime in the various by-products. The first crystal to form was ettringite. It developed at a fast rate due to the ability of this species to solidify. However, over a period of time these crystals deteriorated and new (as yet unidentified) crystals developed in the first crystal's place. Even later, these crystals disappeared and a final crystal structure developed. Also, the stabilized waste exhibited many other permanent crystal phases on the surface of the material.

A final important observation was made. The Scanning Electron Microscope and X-Ray Diffraction did not show the presence of any hazardous metals, either on the surface of the materials or forming their own independent crystal phases. It has yet to be evaluated whether sufficient metals were actually present to have been detected by these microscopic methods.

8/11/95

Evaluation of Crystal Growth in Treated Metal-laden Waste by X-Ray Diffraction and the Scanning Electron Microscope.

The research done by Uschi M. Graham and Thomas L. Robol entitled "Chemical and Mineralogical Transformations of Waste from Dry Flue Gas Desulfurization Techniques" has helped me to develop an idea about crystal growth in cementious material. Their study has helped to enrich my study of crystal growth in stabilized materials because of their worked down on the ettringite crystal and its behaviors in cement. In their project they added flue gas desulfurization residues to the cement and studied the minerals that developed. Also they worked to answer question concerning long term stabilization.

SEM Sample Preparation:

The samples that were made were prepared for the Jeol 35CF Scanning Electron Microscope. The cylinders that were used for making samples were allowed to sit for a period of two weeks in a lab. This did not have an effect on the crystal growth because crystal grow in a very humid enviroment so the hydration can take place. The samples were prepared for use in a Philips X-Pert system were it operates on a theta-two theta scan where the angle on incidence equal to angle of reflection. The samples used in the Scanning Electron Microscope were broken off from the cylinders with a trowel and a mat knife. Once a sample was made the equipment was immediately cleaned so the samples would not become contaminated. The samples chosen to be studied had to be a certain size and had to have a good plane was exposed for the scanning process. The samples were then placed on little platform and placed on a thick ring so the samples could be coated. To hold the sample in place a carbon paint was used to keep the sample from moving while being coated and later scanned. The samples were coated with palladium which had argon gas being pumped into the system. The purpose of coating was to prevent the samples from charging while in the Scanning Electron Microscope.

SEM Examination:

The first sample studied was the Ebensburg/Edison Soil of 7 days. From the XRD patterns the sample contained some quartz, kaolinite, and calcite in its composition. Also the patterns showed some ettringite crystals developing.

The micrograph# 0701 shown at 200x, had a relatively rough looking surface. The large pieces in the background are possibly quartz.

The next micrograph #0702 shown at 1800x. This graph was taken from the side of the little mountain peak from #0701. This graph showed definite crystal development. The thin needles in the picture showed the development of ettringite crystals in that area. Spectrum#1 was taken on the left side area of the micrograph, from this analysis the sample contained high amounts of silica, calcium, and alumina with some sulfur, potassium, titanium, and iron. This area analyzed has some ettringite crystals being developed there.

The micrograph# 0703 shown at 10,000x showed a clear view of the needles in the ettringite early stages of development.

Micrograph# 0704 shown at 2700x was taken from the upper lower left corner of the micrograph# 0701. Spectrum# 2 analyzed the whole micrograph and this area contained high amounts of silica, calcium, and alumina. Also with some high levels of sulfur and iron. The micrograph showed needles developing.

Micrographs # 0705 shown at 9000x. This graph gave a close up of the previous micrograph# 0704 and the needles seem to be quite similar to the needles found in micrograph#

0703.

The micrograph# 0706 shown at 9000x. This area can be found on micrograph# 0704 in the left center of the graph. The needles and the smooth surface possibly could be some sort of calcium structure .

Micrograph# 0707 shown at 1000x. It is located on the most bottom left corner on micrograph# 0701. Spectrum# 3 was taken on the smooth surface of this material and it has high amounts of calcium, sulfur with very few alumina, silica, and iron present. This smooth material was a sort of calcium sulphate/sulphite structure that was able to stay together probably during the mixing process.

The second to the last micrograph# 0708 shown at 5000x. This graph was taken of the step region found on micrograph# 0707. Spectrum# 4 analyzed this step region and that area contained a lot of calcium and sulfur with some alumina, silica, and iron. This graph provides a closer look at the calcium sulphate/sulphite.

The last micrograph taken of the Ebensburg/Edison Soil of 7 days was labeled as # 0709 and it is shown at 2200x. This graph showed some clumped silica in the background of the photo. Spectrum# 5 analyzed the central region of the photo which was composed of high levels of silica with some alumina, calcium, titanium, and iron. The big flakes in the picture were kaolinite flakes.

SEM Examination of 14 days Ebensburg/Edison Soil:

Micrograph# 1401 shown at 100x. The surface seems to be a little coarse. Spectrum #1 showed that the micrograph had high readings of silica, calcium with some alumina, sulfur, potassium, titanium, and iron.

#1402 shown at 1000x. Presented tiny needles and platelet on the surface of the 14 day

Ebensburg/Edison Soil.

#1403 & 1404 shown at 10000x. This graph takes a closer look at the center of the micrograph# 1402. It provided a closer view of the platelet development at that location.

Micrograph# 1405 shown at 1000x. Spectrum # 2 did the analysis of the area in the center of the graph. The spectrum exhibited the high amounts of calcium, silica, and alumina. Also present were sulfur, potassium, iron, and titanium. From this micrograph thin needles could be seen. Spectrum #4 was done on the clumps of material found in the upper lower left corner. This part of the micrograph contained a lot of silica, calcium, alumina with some iron, sulfur, potassium, and titanium.

#1406 shown at 5500x took a closer look at the clumpy material. Spectrum # 3 showed that this material contained silica, alumina with some calcium, potassium, sulfur, iron, titanium. This material could be some sort of alumina silicate material.

Micrograph # 1407 shown at 1800x took another view of the sample. This view should some clumpy material that was kaolinite.

#1408 shown at 1500x showed more clumpy material. Spectrum # 5 contained high levels of silica and calcium with some alumina and iron. This was probably a calcium silicate structure that was analyzed. Spectrum #6 was done on the area located at the lower center of the graph. It contained calcium, silica, alumina, sulfur, iron, titanium, and potassium. Possibly some sort of calcium silicate.

#1409 shown at 1300x has some clay in it. Spectrum # 7 has high amount calcium, silica, alumina, sulfur, titanium, and iron.

CONCLUSION:

The topography of the samples that were analyzed all contained calcium, silica, and alumina with some sulfur and iron. The main thing idea that was pulled away was that the stabilization worked because none of the metals that were considered hazardous showed up on the surface of the stabilized materials. Also the work showed that the stabilized waste was similar to cement because the two contained the same constituents ingredients. Finally the Scanning Electron Microscope displayed the possibilities of having many different structures due to the by-products and hazardous waste unique backgrounds.

X-Ray Diffraction Sample preparation:

The samples were prepared for use in a Philips X-Pert system were it operates on a theta-two theta scan where the angle on incidence equal to angle of reflection. The samples were prepared by breaking pieces of the cylinders into smaller pieces by a trowel. Then the material was crushed by a mortar to a very fine powder because the technique used to analyze the material was Powder Diffraction. Then the sample was placed into a diffraction slide by taping it to a regular microscope slide. Next, the fine powder was packed into the diffraction slide. After that the powder was compacted by the back of the diffraction slides back cover so the powder would be secured. The powder was then tested to see if it was ready by slightly tilting the diffraction slide. Finally, the mortar and the tweezers were cleaned with acetone to prevent the next sample from being contaminated.

Examination:

The results from the Ebensburg/Edison Soil displayed development of ettringite crystals along with calcite and kaolinite. Also it showed high amounts of quartz that was present in the material. The 14 day Ebensburg/ Edison Soil exposed a new phase of crystal growth in this stabilized materials but this phase only lasted for 14 days. The 28 day material was consistent with many of the peaks of the 7 and 14 day samples. However the peaks began to deteriorate and a new phase of crystalline material began to develop.

From the Tidd/Richmond soil 3,7, 14 day XRD Patterns presented development and deterioration of these crystalline materials. The 3 day samples showed the relative beginning stages of the crystalline growth development. By the 7th day the development was significantly different from the 3 day material and the growth of this material was quite evident. But 14 days later the peaks were no longer as great as they were for the 7 day material. Then in the 14 day material new phases began to develop.

CONCLUSION:

The crystalline growth in the stabilized waste were quite dynamic because of the by-products composition. Since the by-products lack the high percentage of ingredients that are found in typical portland cement, the rates in which the crystals developed would be faster especially when studying ettringite crystals since they were the first crystal to develop in this type of material. Overall the development of the crystalline materials insure us that the metals that were considered hazardous will not be able to move about freely because the material was able to solidify.

APPENDIX E

NEWS RELEASE AND RESULTING ARTICLES

University of Pittsburgh

Transforming the Present — Discovering the Future

Office of Public Affairs, 400 Craig Hall, Pittsburgh, PA 15260

CONTACT: Ken Service
TELEPHONE: 412-624-4238

FOR IMMEDIATE RELEASE

PITT RECEIVES DEPARTMENT OF ENERGY CONTRACT TO EVALUATE NEW HAZARDOUS WASTE TREATMENT

PITTSBURGH, June 12 – The U.S. Department of Energy (DOE) has awarded a contract to the University of Pittsburgh School of Engineering Center for Energy Research (ECER) to evaluate the use of by-products from advanced sulfur removal systems in the treatment of metal-laden characteristic hazardous wastes. The two principal subcontractors on the project are Mill Service, Inc. and Dravo Lime Company.

Characteristic metal-laden hazardous waste is currently treated with low-grade lime by Mill Service on a daily basis at its Yukon, PA plant. Lime is also used in scrubber systems at coal-fired electric power plants to remove sulfur dioxide from flue gases. The residue from advanced scrubbers contains some unused lime along with useful chemicals formed when lime and sulfur dioxide react.

The ECER study will evaluate the use of four by-products from advanced sulfur removal systems to treat ten characteristic metal-laden wastes. The treatment should stabilize the hazardous materials in the waste and allow the resulting non-hazardous treated product to be safely disposed in landfills accepting non-hazardous wastes.

- more -

The four by-products to be tested are currently being produced by the AES Thames River Cogeneration Plant near New London, CT; the Carneys Point Cogeneration Plant near Wilmington, DE, and the Ebensburg Power Company plant in Ebensburg, PA. The ten hazardous wastes to be treated will be selected from those regularly received by Mill Service at its Yukon plant.

The project will be conducted in two one-year phases. Phase one will entail a laboratory scale examination to determine the amount of each by-product needed to treat each type of hazardous waste. Phase two will be a commercial scale test by Mill Service of up to ten by-product/hazardous waste combinations identified in phase one as being both technically and economically feasible.

Dravo will be responsible for sampling and analyzing the by-products. Mill Service will sample the wastes and treat them with the by-products. The ECER will analyze the stabilization and solidification of the treated wastes and prepare reports on the project. The principal investigator for the project is James T. Cobb, Jr., associate professor of chemical engineering and director of the Energy Resources Program in Pitt's Engineering School. The project is managed by the U.S. DOE's Morgantown Energy Technology Center through the Office of Technology Development.

- 30 -

6/12/95/kma

Engineers study treatment of waste

By Christopher Lawrence
For The Pitt News

For years, the saying was fight fire with fire. Now, thanks to a Department of Energy contract, engineers at the University of Pittsburgh are rewriting the statement, making it fight waste with waste.

The U.S. Department of Energy has awarded a contract to the University of Pittsburgh School of Engineering Center for Energy Research to evaluate the use of by-products from advanced sulfur removal systems in the treatment of metal-laden hazardous wastes.

"Much of the coal from the western Pennsylvania region contains fairly high levels of sulfur," said Ronald Neufeld, professor of civil engineering and co-principal investigator on the project. "Electric companies that burn this type of coal will produce sulfur dioxide, which is in violation of certain clean air standards."

Electric companies can solve this problem by adding something to the stacks to clean out the sulfur. One way to do this is to add lime into a scrubber, which removes impurities from a gas. The material in the scrubber reacts with the sulfur dioxide, forming calcium sulfite and calcium sulfate. The process produces sludge comprised of ash from the scrubber as well as excess lime.

"It is this excess lime that has commercial value," Neufeld said.

University engineers are taking a look at using the solid waste that contains a lot of excess lime to convert certain kinds of metal-laden hazardous waste into a non-hazardous form.

"We're looking at by-prod-

•*Energy, page 4*

Energy

•From page 1

ucts from four different electrical utility facilities, facilities that would produce an excess of lime solid waste, and we have a matrix of those four with 10 different metal-containing hazardous wastes," Neufeld said.

"Certain soils, incinerator ash, paint residuals and sludge produced by steel mills are among the wastes which, unless treated, are considered hazardous," said James Cobb, principal investigator on the project and director of the Energy Resources Program in Pitt's Engineering School.

There are two principal subcontractors on the project — Mill Service Inc., a waste treatment facility, and the Dravo Lime Company.

The 10 hazardous wastes to be treated were selected from those regularly received by Mill Service. The treatment should stabilize the hazardous material in the waste and allow the resulting non-hazardous treated product to be safely disposed of in landfills accepting non-hazardous wastes.

The project will be conducted in two one-year phases. Phase one, conducted over the past year, entailed a laboratory scale examination to determine the amount of each by-product needed to treat each type of hazardous waste. Phase two, which is about to begin, will be a commercial scale test by Mill Service of up to 10 by-product/hazardous waste combinations identified in phase one as being both technically and economically feasible.

"Certain soils, incinerator ash, paint residuals and sludge produced by steel mills are among the wastes which, unless treated, are considered hazardous."

—James Cobb

Director of the Energy Resources Program in Pitt's Engineering School

"The idea of using lime for stabilization purposes is not a new one," Cobb said. "It's been around for a while."

"What's innovative about the project is the source of the lime — the 'dirty lime' coming from clean coal technology applications," Neufeld said.

"What makes this project so interesting is that there is a combination of theoretical studies and fundamental studies taking place in the Environmental Engineering Program and the Chemical Engineering and Energy Resources Department, as well as larger scale activities taking place out in the field under the auspices of a private sector participant," Neufeld said.

Pitt competed with other universities and companies for the Department of Energy contract.

"We won it based on a combination of our technical merit and the ideas set forth in our proposal," Neufeld said. "This was a competitive procurement that we managed to win."

Pittsburgh Business Times

RECORD

CONTRACTS

The University of Pittsburgh's School of Engineering, through its Center for Energy Research, was awarded a contract by the U.S. Department of Energy to study ways to stabilize hazardous wastes into storable non-hazardous waste. The principal subcontractors on the project are **Mill Service Inc.** and **Dravo Lime Co.**

VOLUME 27 • NUMBER 23 JULY 20, 1995

UNIVERSITY **TIMES**

RESEARCH NOTES

Engineering school awarded contract from DOE

The U.S. Department of Energy has awarded a contract to the Pitt School of Engineering Center for Energy Research to evaluate the use of by-products from advanced sulfur removal systems in treating metal-laden characteristic hazardous wastes.